(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 July 2003 (17.07.2003)

PCT

(10) International Publication Number
WO 03/057632 A1

(51) International Patent Classification[7]: C02F 3/12, 3/30, 1/44

(21) International Application Number: PCT/EP02/00269

(22) International Filing Date: 7 January 2002 (07.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants *(for all designated States except US)*: **BERLINER WASSER BETRIEBE** [DE/DE]; Neue Judenstrasse 1, 10179 Berlin (DE). **COMPAGNIE GENERALE DES EAUX** [FR/FR]; 52, rue d'Anjou, F-75008 Paris (FR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **GNIRSS, Regina** [DE/DE]; Gernsheimstrasse 30A, 12247 Berlin (DE). **LESJEAN, Boris** [DE/DE]; Torstrasse 176, 10115 Berlin (DE).

(74) Agent: **VIDON, Patrice**; Cabinet Patrice Vidon, Le Nobel - Bât. A, 2, allée Antoine Becquerel, B.P. 90333, F-35703 Rennes 7 (FR).

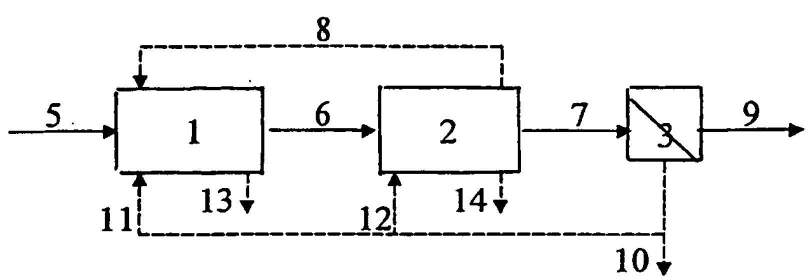
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BIOLOGICAL TREATMENT PROCESS INVOLVING POST-DENITRIFICATION MECHANISM AND A MEMBRANE FILTER



(57) Abstract: A process for treating water to remove nitrogen to required low treatment level, using post-denitrification mechanisms without addition of carbon sources, and characterized in that it comprises the steps of (h) providing an aerobic zone (1) having an aerobic mixed liquor having organisms which degrade the carbonaceous matter and nitrify the aerobic mixed liquor; (ii) providing an anoxic zone (2) having an anoxic mixid liquor having organisms which denitrify the anoxic mixed liquor without any need of additional carbon sources; (j) flowing water to be treated into said aerobic zone (1); (k) flowing aerobic mixed liquor into said anoxic zone (2); (l) contacting anoxic mixed liquor against the feed side of a membrane filter (3); (m) producing a treated effluent lean in nitrogen, BOD, COD suspended solids and organisms from a permeate side of the membrane filter (3); and (n) removing some or all of the material rejected by the membrane filter (3) from the process, wherein the steps above are performed substantially continuously and substantially simultaneously.

WO 03/057632 A1

BIOLOGICAL TREATMENT PROCESS INVOLVING POST-DENITRIFICATION MECHANISM AND A MEMBRANE FILTER

The invention deals with biological water treatment process. More precisely, the invention deals with a Membrane Bioreactor (MBR) technology.

State of the art

The Membrane Bioreactor (MBR) technology combines the activated sludge treatment technology with membrane filtration. It was developed in the 80's and has been widely used for treatment of industrial wastewater and municipal wastewater.

Compared to traditional activated sludge treatment technology, MBR technology offers the following advantages: advanced treatment (COD, Nitrogen, Pathogens, etc), robustness and compactness.

Traditionally, MBR systems are operated with high sludge age (solid retention time), and low mass organic load. These conditions favour ammonification and nitrification mechanisms in the aerobic zone (biological transformations of organic nitrogen compounds to ammonia, and ammonia to nitrate via nitrite). When denitrification is required (nitrogen removal mechanism, through the transformation of nitrate to nitrogen gaz), an anoxic zone is added.

To the inventors knowledge, in MBR systems, the anoxic zone was to date always implemented *in pre-denitrification* configurations (anoxic zone ahead of the aerobic zone), with a mixed liquor recirculation loop from the aerobic zone to the anoxic zone. This configuration originated from conventional activated sludge systems, that are traditionally designed with pre-denitrification process. This is expected to offer the following advantages :

(i) use of biodegradable organic matter available in the anoxic zone to improve denitrification rate, hence reduce the required volume of biological reactor, and

(ii) use of oxidation capacity of nitrate to degrade part of the organic matter, hence to reduce oxygen demand and to achieve saving in aeration requirement.

The inventors identify these advantages as non-substantial with MBR systems for the following reasons:

(i) due to the low mass organic load of MBR processes, the amount of biodegradable organic matter available for denitrification in the anoxic zone is very low, hence the denitrification rate is close to the *endogeneous denitrification rate* (minimum denitrification rate observed when no organic matter is available), and

(ii) the aeration requirement of MBR systems are mainly related to the aeration of the membrane filter in order to limit the fouling of the membrane, and not to the oxygen requirement of the mixed liquor, therefore the reduction in oxygen demand due to the pre-denitrification mode is not expected to reduce much the aeration requirement of the whole systems.

The pre-denitrification configuration appears to be not well-adapted to MBR technology. In contrast, post-denitrification process configurations can be in some cases favourable to MBR systems, and improve their performances.

It is to be noted that post-denitrification is reported in the literature for conventional activated sludge systems, but always while resorting to the addition of carbon sources (Wilson T.E. and Newton D., "Brewery Wastes as a Carbon Source for Denitrification at Tampa, Florida, May 1973", presented at the 28th Annual Purdue Industrial Waste Conference ; Mitsdörfer R. and Gerhart U., "Nachgeschältete Methanol-Denitrifikation im Sandfilter", gwf 133, 1992, Heft 9). The inventors claim that unlike conventional sludge systems, the addition of carbon sources is not required to achieve efficient post-denitrification with membrane bioreactor. Nevertheless, it will be understood that, despite the fact that the addition of a carbon source is not compulsory during the implementation of the present invention, it will be possible to add such a carbon source without drawback.

Description of the invention

This description is made in reference to figures 1 to 5.

The following definitions will be used.

Type of membrane filter: The expression "membrane filter" refers to any type of membrane microfiltration or ultrafiltration device, with pore size ranging from 10nm to 10μm.

Source of water: The expression "water to be treated" refers to any type of waste water source subject to any pretreatment (municipal or industrial wastewater, screened or presettled, etc).

Design of biological zones: The expressions "anaerobic zone", "anoxic zone" and "aerobic zone" refers to any type of biological reactor (plug-flow, well-mixed, or non-defined), maintained respectively under anaerobic, anoxic and aerobic conditions. The term "zone" refers to one or a succession of several biological reactors containing a biological mixed liquor. The invention is also valid for alternative reactor geometries, such as carrousel or meander reactors, which ensure successive aerobic and anoxic conditions of the mixed liquor.

Aerobic conditions: The term "aerobic mixed liquor" refers to any mixed liquor in which the level of dissolved oxygen would be maintained over 0,1 mg/L.

Anoxic conditions: The term "anoxic mixed liquor" refers to any mixed liquor in which the level of dissolved oxygen would be maintained below 0,1 mg/L, and with a presence of nitrate.

Anaerobic conditions: The term "anaerobic mixed liquor" refers to any mixed liquor in which the level of dissolved oxygen would be maintained below 0,1 mg/L, and the level of nitrate would be maintained below 0.1 mg/L.

Source of carbon: The expression "source of carbon" refers to any material containing a carbon substrate which is made available for organisms. This includes, but is not limited to, raw water and derivatives, chemicals such as methanol, acetate, glucose, etc, or any industrial solid or liquid product (molasses, etc).

The invention relates to a process configuration for biologically treating waste water. It involves a biological reactor set-up with a post-denitrification zone and a membrane filter. The process includes a minimum of two distinct zones, an aerobic zone (1), and an anoxic zone (2), containing an aerobic and an anoxic mixed liquid liquor, and a membrane filter (3). The membrane filter can be set up in an external zone (Figure 1), immersed in the anoxic zone (Figure 2), or immersed in an additional aerobic zone (4), (Figure 3). Water to be treated (5) flows first into the aerobic zone (1). Aerobic mixed liquor (6) flows to the anoxic zone (2). Post-denitrification of nitrate NO3 occurs in this anoxic zone. Anoxic mixed liquor flows (2) to the feed side of the membrane filter (3), and optionally back (8) to the aerobic zone (1). The membrane filter treats the mixed liquor to produce a treated effluent (9) lean in nitrogen, BOD, COD and organisms at a permeate side of the membrane filter and a liquid rich in rejected solids and organisms. Some or all of the material rejected by the membrane filter is removed from the process either directly (10) or by returning the material rejected by the membrane filter to one of the zones (11, 12) and wasting the mixed liquor from the aerobic or the anoxic zone (13, 14). In a first variation (Figure 4), an anaerobic zone (15), containing an anaerobic mixed liquor, is added in front of the aerobic zone (1), in order to achieve enhanced biological phosphorous removal. In this variation, mixed liquor flows from the anoxic zone to the anaerobic zone (16). A pre-fermenter zone, containing the water to be treated, can be also optionally added (17), in order to improve the characteristics of the water to be treated and to foster enhanced biological phosphorous removal. In a second variation (Figure 5), a source of carbon (18) is added in the anoxic zone, in order to improve the post-denitrification capacity. Other chemicals or products can be also added at specific places of the process according to needs (such as addition of coagulant to precipitate phosphorous, addition of acid or base to adjust pH, or addition of polymer to enhance performances of membrane filter).

The process according to the invention shows the following advantages.

Compared to traditional configurations of MBR systems, operating in pre-denitrification mode, the post-denitrification configuration is expected to achieve better effluent quality for nitrate (typically less than 5 mg N/L) and total nitrogen (typically less than 10 mg N/L). When an anaerobic zone is added (first variation), low total phosphorous content is also expected in the effluent (typically less than 1 mg N/L). The process will be also more compact, and will require lower mixed liquor flow rates, therefore lower power requirement. In addition, a simpler control strategy to optimise nitrogen removal is expected (except when carbon source is added).

This system can be operated under the following ranges of operation conditions:

Solid retention time (sludge age)	10 – 50 days
Hydraulic retention time	10 – 70h
Mixed liquor suspended solid (sludge concentration)	5 – 20 g/L
Mass organic load	0.05 – 0.25 kgCOD / kgMVS.d
Mixed liquor flow rate from membrane filter to aerobic zone (11)	50 – 500% (re. unit throughflow)
Mixed liquor flow rate from anoxic to anaerobic zone (16)	25 – 200% (re. unit throughflow)

Examples

A continuous process pilot plant was set up to confirm the advantages of this invention on pre-denitrification processes traditionally used with membrane bio-reactors. The post-denitrification reactor was set up according to Figure 4 with a separated aerated membrane filter system, whereas the pre-denitrification reactor consisted in the succession of anaerobic zone, anoxic zone and aerobic zone, with the same membrane system. Sludge retention time (SRT) was kept constant at 15 days and 25 days during further trials. The reactors were continuously fed with a constant flowrate of degritted municipal wastewater. The hydraulic retention times (HRTs) of each zone are given in Table 1 below.

Table 1

Post-denitrification reactor	Anaerobic zone	Aerobic zone	Anoxic zone	Aerated filter chamber	Overall bioreactor
Operating HRTs	3.7h	4.3h	9.7h	3.3h	21h
Pre-denitrification reactor	Anaerobic zone	Anoxic zone	Aerobic zone	Aerated filter chamber	Overall bioreactor
Operating HRTs	3.7h	8.5h	5.5h	3.3h	21h

After 2-3 sludge ages of continuous operation, an extensive analysis campaign was carried out over 2 weeks. 24h average sample were taken everyday from each reactor affluent and analysed. Table 2 presents the average results of these analyses for the trials undertaken with 15 day sludge age.

Table 2

	COD (mg O_2/L)	NH_4-N (mg N/L)	NO_3-N (mg N/L)	NT (mg N/L)	PT (mg P/L)
Post-denitrification reactor					
Influent	653	39.0	0.33	60.0	8.4
Effluent	31.4	0.05	4.2	5.9	0.07
Removal	95.2%	99.9%	-	90,2.0%	99.1%
Pre-denitrification reactor					
Influent	1088	41.3	0.42	69.7	10.5
Effluent	35.7	0.49	6.0	9.2	0.10
Removal	96.7%	98.8%	-	86.8%	99.0%

Both experiments were undertaken under the same operation conditions and for a similar quality of raw water. Table 2 shows that for COD and PT parameters the purification performances of the post-denitrification system are comparable to the pre-denitrification configuration, or slightly better. The difference between both system is greater for nitrogen parameters. The post-denitrification reactor achieved greater degree of ammonia and nitrogen removal, and lower nitrate values in the effluent. In particular, the post-denitrification reactor achieved 90,2% nitrogen removal, producing a 5.9 mg N/L effluent, whereas the pre-denitrification reactor achieved only around 87% with 9.2 mg N/L.

CLAIMS

1. A method for treating water to remove nitrogen to required low treatment level, using post-denitrification mechanisms without addition of carbon sources, and characterized in that it comprises the steps of :

    (a) providing an aerobic zone (1) having an aerobic mixed liquor having organisms which degrade the carbonaceous matter and nitrify the aerobic mixed liquor;

    (b) providing an anoxic zone (2) having an anoxic mixed liquor having organisms which denitrify the anoxic mixed liquor without any need of additional carbon sources;

    (c) flowing water to be treated into said aerobic zone (1);

    (d) flowing aerobic mixed liquor into said anoxic zone (2);

    (e) contacting anoxic mixed liquor against the feed side of a membrane filter (3);

    (f) producing a treated effluent lean in nitrogen, BOD, COD suspended solids and organisms from a permeate side of the membrane filter (3); and

    (g) removing some or all of the material rejected by the membrane filter (3) from the process,

    said steps being performed substantially continuously and simultaneously.

2. A method for treating water to remove nitrogen to required low treatment level, using post-denitrification mechanisms without addition of carbon sources and comprising the steps of

    (a) providing an aerobic zone (1) having an aerobic mixed liquor having organisms which degrade the carbonaceous matter and nitrify the aerobic mixed liquor;

(b) providing an anoxic zone (2) having an anoxic mixed liquor having organisms which denitrify the anoxic mixed liquor without any need of additional carbon sources;

(c) flowing water to be treated into said aerobic zone (1);

(d) flowing aerobic mixed liquor into said anoxic zone(2);

(e) flowing the anoxic mixed liquor into an aerated zone (4) containing a membrane filter;

(f) producing a treated effluent lean in nitrogen, BOD, COD suspended solids and organisms from a permeate side of the membrane filter (3); and

(g) removing some or all of the material rejected by the membrane filter (3) from the process,

wherein the steps above are performed substantially continuously and substantially simultaneously.

3. The method of anyone of claims 1 or 2 wherein said anoxic mixed liquor flows to the aerobic zone.

4. The method of anyone of claims 1 to 3 wherein material rejected by the membrane filter (3) is also mixed with said aerobic mixed liquor.

5. The method of anyone of claims 1 tto 3 wherein material rejected by the membrane filter (3) is also mixed with said anoxic mixed liquor.

6. The method of anyone of claims 4 or 5 wherein the step of removing material rejected by the membrane filter (3) from the process is accomplished by removing said aerobic mixed liquor containing material rejected by the membrane filter (3).

7. The method of anyone of claims 4 or 5 wherein the step of removing material rejected by the membrane filter (3) from the process is accomplished by removing said anoxic mixed liquor containing material rejected by the membrane filter (3).

8. The method of anyone of claims 1 to 7 inclusive further comprising the steps of

- providing an anerobic (15) zone having an anaerobic mixed liquor;
- (flowing water to be treated into said anaerobic zone (15);
- flowing anaerobic mixed liquor into said aerobic zone (1); and
- flowing anoxic mixed liquor into said anoxic zone (2).

9. The method of claim 8 further comprising the steps of

- providing a pre-fermenter zone (17) containing fermented water;
- flowing water to be treated into the pre-fermenter (17) zone; and
- flowing the fermented water into the anaerobic zone (15).

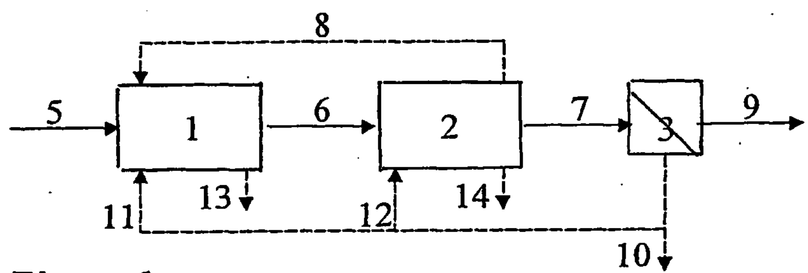


Figure 1

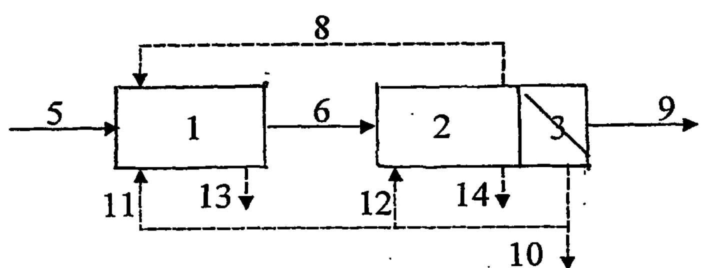


Figure 2

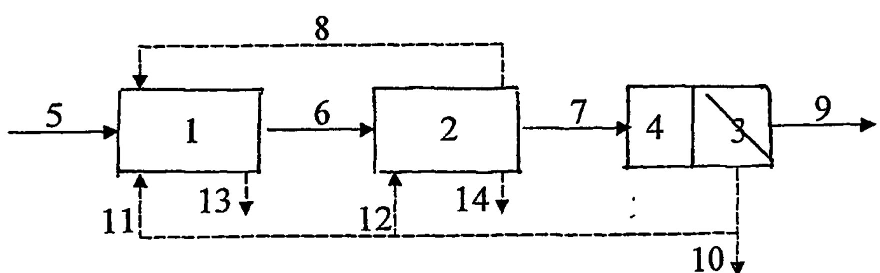


Figure 3

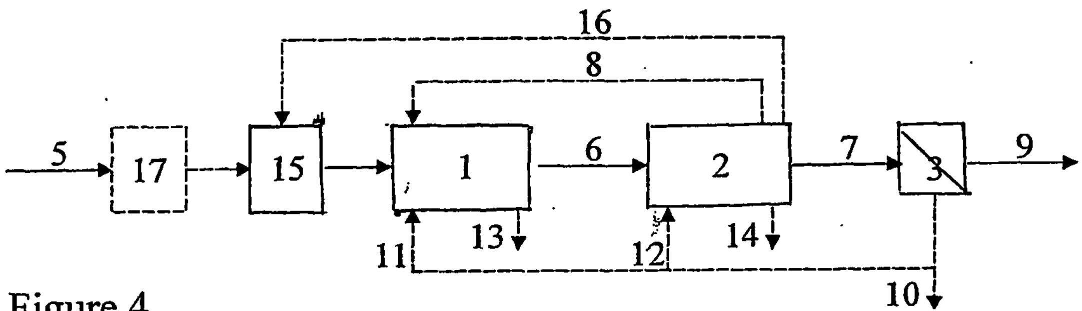


Figure 4

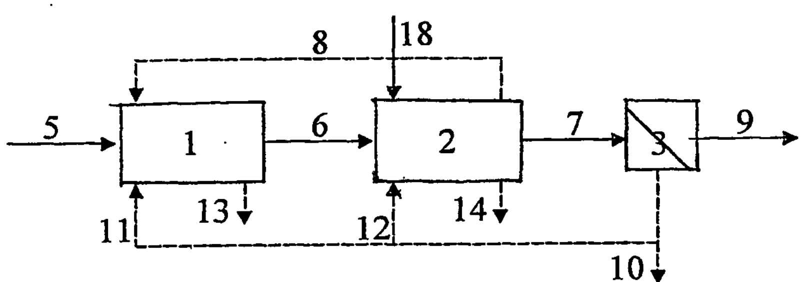


Figure 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/00269

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F3/12 C02F3/30 C02F1/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 861 808 A (KURARAY CO) 2 September 1998 (1998-09-02) page 21, line 25-41; figure 4	1,4,5
X	EP 0 761 607 A (HITACHI PLANT ENG & CONSTR CO) 12 March 1997 (1997-03-12) page 15, line 50 -page 17, line 14; figure 16 page 7, line 9-15	1,3,4
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 02, 30 January 1998 (1998-01-30) -& JP 09 271796 A (KUBOTA CORP), 21 October 1997 (1997-10-21) abstract	1,2,8

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2002	10/10/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Borello, E

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/00269

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 137 (C-582), 5 April 1989 (1989-04-05) -& JP 63 302996 A (EBARA INFILCO CO LTD;OTHERS: 01), 9 December 1988 (1988-12-09) abstract ---	1,2,8
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 08, 6 October 2000 (2000-10-06) -& JP 2000 126793 A (MITSUBISHI HEAVY IND LTD), 9 May 2000 (2000-05-09) abstract -----	1,2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/00269

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0861808 A	02-09-1998	CN 1199712 A	25-11-1998
		EP 0861808 A2	02-09-1998
		JP 11042497 A	16-02-1999
		US 6007712 A	28-12-1999
EP 0761607 A	12-03-1997	JP 3180891 B2	25-06-2001
		JP 9047787 A	18-02-1997
		JP 3252887 B2	04-02-2002
		JP 9047788 A	18-02-1997
		JP 3252888 B2	04-02-2002
		JP 9075984 A	25-03-1997
		CA 2181481 A1	11-02-1997
		DE 69616216 D1	29-11-2001
		DE 69616216 T2	02-05-2002
		EP 0761607 A1	12-03-1997
		US 5849180 A	15-12-1998
		US 5997736 A	07-12-1999
		US 6033569 A	07-03-2000
		US 5876603 A	02-03-1999
JP 09271796 A	21-10-1997	JP 3285754 B2	27-05-2002
JP 63302996 A	09-12-1988	JP 1673361 C	12-06-1992
		JP 3025239 B	05-04-1991
JP 2000126793 A	09-05-2000	NONE	